Infrared Spectra of Polyacrylonitrile Polymerized by Gamma-irradiation at Low Temperatures

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In order to study the effect of polymerization condition on the infrared spectrum of polyacrylonitrile, acrylonitrile was polymerized in bulk and in various solutions by gamma-irradiation at low temperatures and it was found that the intensities of absorption bands at 1675 and 2030 cm^{-1} vary according to the polymerization conditions, i. e., the solvent species and the irradiation temperatures. Figure 1 shows the infrared spectra in the 1500~2500 cm^{-1} region obtained from the potassium bromide disks of some different polyacrylonitrile samples. Samples A, B and C were obtained by gamma-irradiation of pure acrylonitrile at 17, -78.5 and -196°C, respectively. Figure 2 shows that of sample D which was obtained by gamma-irradiation of acrylonitrile in triethylamine solution at -78.5°C. As may be seen in these figures, the absorption band at 1675 cm^{-1} is much more intense in sample D than in samples A and B and this band is not observed at all in sample C. On the other hand, the band at 2030 cm^{-1} which is not observed in samples A, C and D is intense in sample B. The band at 1675 cm^{-1} was assigned by Liang and Krimm(1) to a vibration of an impurity. On the basis of the behavior of this band, it is sure that this band should be assigned to a vibration characteristic of a special structure of polyacrylonitrile itself.

From the copolymerization studies of acrylonitrile and styrene by gamma-irradiation at

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1) C. Y. Liang and S. Krimm, *J. Polymer Sci.*, **31**, 513 (1958).

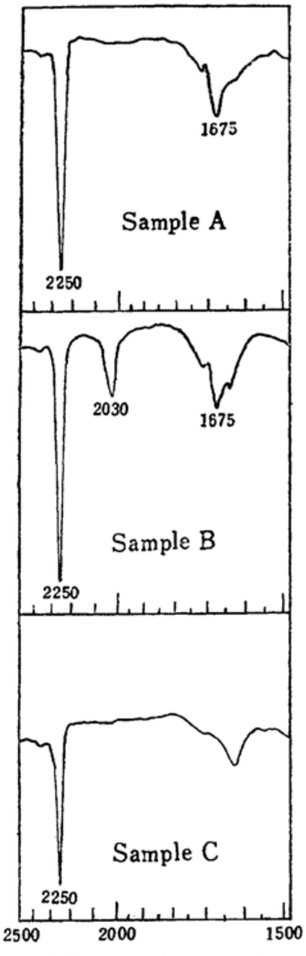


Fig. 1. Infrared spectra of polyacrylonitrile obtained by gamma-irradiation. Samples A, B and C were polymerized in bulk at 17, −78.5 and −196°C, respectively.

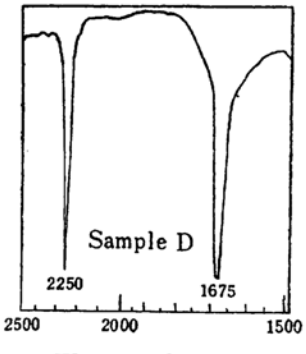


Fig. 2. Infrared spectrum of polyacrylonitrile obtained by gamma-irradiation in triethylamine solution at −78.5°C.

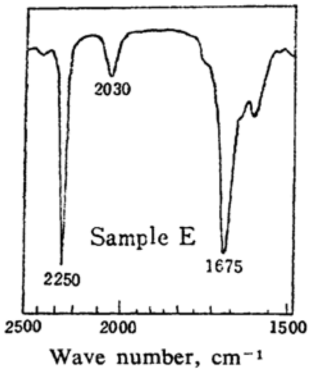
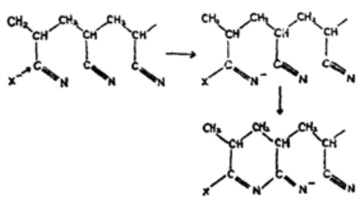


Fig. 3. Infrared spectrum of polyacrylonitrile obtained by gamma-irradiation in *N*, *N*-dimethylformamide solution at −78.5°C.

−78.5°C[2], it was shown that the polymerization proceeds in bulk by a free-radical mechanism, on the other hand, in dilute organic solutions predominantly by an anionic mechanism. In view of these facts, it can be considered reasonably that the band at 2030 cm^{-1} is due to the keteneimine linkage, as has been described previously[3], and the band at 1675 cm^{-1} is due to the C=N linkage which comes from a reaction by an anionic mechanism. The latter band is also intense in the spectrum of polymer obtained in dimethylformamide solution as shown in Fig. 3.

In order to determine whether the C=N linkage is formed by the action of radiations on the polymer or is formed by the polymerization processes themselves, the polymer sample C which has no absorption at 1675 cm^{-1} was dissolved in dimethyl formamide and then irradiated at −78.5°C. In the infrared spectrum of the irradiated polymer the band at 1675 cm^{-1} was observed to be as intense as that of the sample D. When this polymer solution was irradiated at room temperature, any increase of the absorption at 1675 cm^{-1} was not observed in the spectrum of the irradiated polymer. These facts indicate that the formation of C=N linkage is due to the action of radiations on the polymer in these solutions at low temperatures.

From the above consideration, the following reaction to give the conjugated C=N linkage to the polymer can be assumed to occur by gamma-irradiation at low temperatures,



where X$^-$ denotes an anion formed by the irradiation of solvent molecule at low temperatures. The formation of the same structure was also assumed recently in an anionic

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[2] Y. Tsuda, *J. Polymer Sci.*, in press.

[3] C. S. H. Chen, N. Colthup, W. Deichert and R. L. Webb, *J. Polymer Sci.*, **45**, 247 (1960).

polymerization of acrylonitrile[4]. This reaction proceeds easily by an anionic mechanism as shown above, however, it seems that the similar reaction proceeds also by a free-radical mechanism, the rate of formation being very small, as shown by the presence of the weak absorption at 1675 cm^{-1} in the spectrum of polymer obtained in bulk.

The infrared spectra of the polymer samples were obtained using Perkin-Elmer model 21 spectrophotometer. The gamma-rays of $^{60}\mathrm{Co}$ were used for the gamma-irradiation at the dose rate of 4×10^{4} r/hr.

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[4] P. Claes and G. Smets, *Makromol. Chem.*, **44**, 212 (1961).